

Temperature-induced shift of the exciton absorption band in InP/ZnS quantum dots

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Abstract: Using the second-order derivative spectrophotometry method, we have determined the energy of optical transitions of colloidal InP/ZnS core-shell quantum dots at room temperature: $E_1 = 2.60$ eV corresponds to a first exciton absorption peak of the InP core, $E_2 = 4.70$ eV appears to meet the processes in the ZnS shell. We have investigated $E_1(T)$ temperature dependence within 6.5 – 296 K range for the first time. The obtained experimental data have been approximated by means of a linear model and Fan's expression. Also, it has been shown that the interaction between excitons and longitudinal acoustic phonons causes the energy E_1 to change with temperature. In this case, the peak's FWHM remains invariant and amounts to 0.39 eV, which indicates the inhomogeneous broadening character and a high degree of static disorder in the ensemble of the quantum dots studied.

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Colloidal quantum dots (QDs) or semiconductor nanocrystals currently attract the attention of researchers both due to their unique luminescent properties and due to the possibility of finely tuning the optical characteristics for modern light-emitting devices, solar cells, photocatalysts, etc. to be designed [1–7]. QDs based on compounds of III-V groups are of special interest because of containing no toxic elements (Cd, Pb, and Hg). Consequently, they can be widely utilized, e.g. for creating phosphors, biosensors, biomarkers, and various biocompatible applications [8]. From this viewpoint, one of the promising functional media is InP nanocrystals coated with zinc sulfide shell [9]. It is known that, determined by the first exciton peak position in the optical absorption spectra, the energy gap in InP/ZnS can be varied over a wide range by changing the QDs' size [10]. Another factor that influences this quantity is temperature. In this case, analysis of the temperature dependence gives fundamental quantitative information concerning the electron-phonon interaction parameters. To date, there are studies reporting the temperature changes in photoluminescence spectra (PL) of InP/ZnS semiconductor nanocrystals [11, 12]. This paper analyzes the behavior of the optical absorption spectra (OA) ranged from 6.5 to 296 K in the InP/ZnS core-shell quantum dots.

The structure of the InP/ZnS QDs studied (FSUE "The Research Institute of Applied Acoustics", Dubna, as a manufacturer) was three-layered: the core made of InP, the shell made of ZnS, and the coating of a modified polyacrylic acid. According to the manufacturer, QDs have an average diameter of 2.1 nm and are characterized by cubic zinc blende structure. Initial samples of the nanocrystals consisted of a concentrated aqueous colloidal solution ($C = 40$ g/l). Their emission band has 513 nm peak position with a 40 nm full width at half maximum (FWHM); the luminescence quantum yield amounted to 13% (according to the manufacturer). By successively diluting with distilled water, we prepared a concentration series in the range of $C = 40 - 0.04$ g/l. Changes in the optical absorption spectra of the colloidal solutions with different concentrations of QDs were measured at room temperature using a Shimadzu UV-2450 spectrophotometer in a quartz cuvette with 1 cm optical path. The

stability of the resulting solutions was confirmed by a linear concentration dependence of the measured absorbance (A) at wavelengths of 260 nm, 370 nm, and 470 nm.

To establish the absorption-temperature dependence of the nanocrystals, we used dry InP/ZnS precipitate produced by physical deposition of the starting colloidal solution on a quartz substrate with a thickness of 1 mm at room temperature. The OA spectra were measured at $T = 6.5 - 296$ K using a combined unit based on a Shimadzu UV-2450 spectrophotometer and a Janis closed cycle refrigerator system, model CCS-100/204N, equipped with a DT-670B-CU temperature sensor. A HiCube 80 Eco turbo pumping station maintained vacuum inside the cryostat ($7 \cdot 10^{-5}$ mbar). The OA spectra were registered at pre-assigned temperature values: 6.5 K, over the range from 10 to 100 K in 10 K, and in the range of 100 – 296 K with a temperature step of 20 K. During the measurements, the spectral slit width amounted to 2 nm; the sampling interval was 0.1 nm.

Figure 1(a) displays the OA spectra for the QDs solution series tested. As can be seen, the quantity A declines monotonically with decreasing concentration of InP/ZnS. Also, we can observe the absorption features over a wide spectral range of 200 – 700 nm. At the same time, the curves 2 – 4 have a peak of E_1 in the range of 480 – 450 nm, the curves 5 – 7 reveal a shoulder of E_2 in the range of 270 – 240 nm. Figure 1(b) shows the OA spectra of the InP/ZnS quantum dots, measured at various temperatures. As the plot suggests, the first exciton absorption band, when cooled, shifts towards higher energies, and the corresponding optical density grows. The figure insert illustrates these changes in more detail.

It is worth noting that against the idealized theoretical description, the absorption of the real QDs manifests itself in the form of peaks and/or shoulders at a monotonically increasing background. This is because, presumably, the corresponding bulk density of states, scattering processes, etc. makes a contribution [10, 13]. In this regard, the approaches of derivative spectrophotometry can be applied for the optical transitions to be characterized and for the positions of hidden absorption bands to be determined [14].

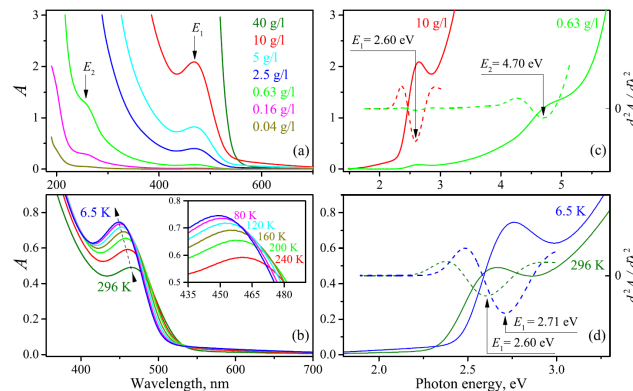


Fig. 1. Optical absorption spectra of InP/ZnS for various concentrations (a) and temperatures (b). Second derivative spectra for various concentrations (c) and temperatures (d).

This paper investigates all of the experimentally obtained OA spectra of the nanocrystals using the second derivative method. As can be noticed from Fig. 1(c), arrows indicate the optical transition energy estimates made on the positions of $d^2A/d\lambda^2$ minima (dashed lines). At room temperature, the energies are: $E_1 = 2.60 \pm 0.02$ eV and $E_2 = 4.70 \pm 0.02$ eV. It should be emphasized that the values calculated are unchangeable for the colloidal quantum dot solutions with different C . The foregoing provides an additional proof of the stability of the concentration series examined.

According to the independent data, the peak of E_1 can be attributed to the first exciton absorption band of indium phosphide. Due to the quantum confinement effect, its energy has a significant blue shift with respect to the forbidden gap of bulk InP (1.34 eV at $T = 290$ K

[15]). The value of E_2 falls within the same energy range of 4.47 – 4.82 eV as in [16] for the forbidden gap of zinc sulfide nanocrystalline powders. Thus, the specified optical transition can be attributed to the ZnS shell. Note that a detailed analysis of this issue requires further research that goes beyond the scope of this paper.

To determine the energy E_1 at various temperatures, we also employed the second derivative method, see Fig. 1(d). The dependence is presented in Fig. 2(a). It can be seen that the magnitude of E_1 rises as T decreases and behaves similarly to the temperature-induced change in the optical gap in bulk semiconductors [15, 17].

The experimental curves of $E_1(T)$ to be quantitatively analyzed necessitated appealing to Fan's expression for temperature behavior of the forbidden gap width in crystals [17, 18]:

$$E_1(T) = E_1(0) - A_F \langle n_s \rangle, \quad \text{where} \quad \langle n_s \rangle = [\exp(\hbar\omega / kT) - 1]^{-1} \quad (1)$$

as well as to a semi-empirical linear model:

$$E_1(T) = E_1(0) - \beta T. \quad (2)$$

Here $E_1(0)$ is the energy of the optical transition at 0 K, eV; A_F is the Fan's parameter that depends on the microscopic properties of materials [18], eV; $\langle n_s \rangle$ is the Bose-Einstein factor for phonons with mean energy $\hbar\omega$; k is the Boltzmann constant, eV/K; β is the energy level shift temperature coefficient (the analog of the temperature coefficient of the forbidden gap in bulk materials), eV/K. As previously demonstrated in [17], in the limit of high temperatures ($kT \gg \hbar\omega$), the relation (1) reduces to (2), with the temperature coefficient being written as:

$$\beta_\infty = A_F \frac{k}{\hbar\omega}. \quad (3)$$

The known papers describe independently similar dependencies by other relations. To explain how temperature affects PL peak maxima of InP/ZnS nanocrystals of different sizes the works [11, 12] apply a relation proposed in [19]:

$$E_1(T) = E_1(0) - 2S\hbar\omega \langle n_s \rangle \quad (4)$$

where S is the Huang-Rhys factor. Having compared the expressions (1) and (4), it is easy to see that $A_F = 2S\hbar\omega$. The paper [20] analyzes the temperature-dependent change in the energy of different optical transitions estimated by PL excitation spectra in wurtzite indium phosphide nanowires. In mentioned work, the experimental data are approximated by the following expression [21]:

$$E_1(T) = E_B - a - 2a \langle n_s \rangle \quad (5)$$

where $E_B - a = E_1(0)$, a is a parameter characterizing the electron-phonon interaction strength. Comparing the expressions (1) and (5), we arrive at $A_F = 2a$. Thus, it is obvious that the expressions (1), (4), and (5) are analogous to each other. They make it possible to describe temperature dependencies of OA and PL in materials and to extract quantitative information on the electron-phonon interaction which governs, in a significant degree, the energy-level shifts observable. In general, according to [22, 23] energy level positions in quantum dots are influenced by 4 temperature-dependent factors: dilation of the lattice, thermal expansion of the envelope function, mechanical strain, and electron-phonon coupling. However, the latter contribution dominates both for quantum dots [22] and bulk materials [17].

Figure 2(a) shows the approximation of the energy shift dependence $\Delta E_1(T) = E_1(T) - E_1(0)$ using Fan's relation (a solid line) and a linear model (a dashed line). Table 1 summarizes the parameters obtained compared to independent literature data. As can be seen, the calculated value corresponds to $\hbar\omega = 15.5$ meV energy of longitudinal acoustic (LA)

modes in bulk InP [24] and is consistent with the results for the temperature behavior of the exciton absorption peak in InP single crystals [25]. Also, the $\hbar\omega$ and A_F values match the values for the InP nanowires and the InP/ZnS quantum dots. At the same time, the energy values at zero temperature are different due to the size effect.

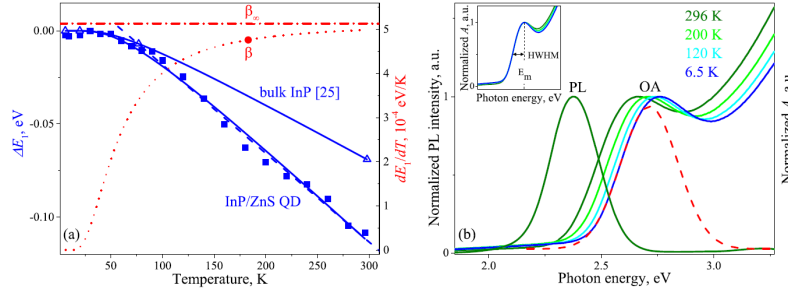


Fig. 2. Energy shift and broadening analysis of exciton absorption band: (a) ΔE_1 temperature dependence – blue square symbols are our experimental estimates, blue triangle symbols are experimental estimates from [25]; (b) normalized PL and OA spectra of the InP/ZnS QDs.

In Fig. 2(a) the dotted line represents the dependence dE_1/dT that characterizes the change in the temperature coefficient β . The dash-dotted line corresponds to the level of $\beta_\infty = 5.13 \cdot 10^{-4}$ eV/K calculated by the expression (3). The value of $\beta = 4.76 \cdot 10^{-4}$ eV/K (shown as a red circle) was calculated based on the approximation of $E_1(T)$ in the range of 90 – 296 K by the expression (2) (a dashed line in Fig. 2(a)) and matches the reference data for bulk InP ($4.6 \cdot 10^{-4}$ eV/K [15]). In general case, the values of β depend on the T -interval applied for the linear approximation. Since the relation $\beta \approx \beta_\infty$ is fulfilled, it can be spoken that the interval of 90 – 296 K considered for the QDs tested fully satisfies the high temperature condition $kT \gg \hbar\omega$.

Table 1. Parameters of the temperature dependence of $E_1(T)$.

Material	$E_1(0)$, eV	A_F , eV	$\hbar\omega$, meV	β_∞ , 10^{-4} eV/K	FWHM, eV
InP/ZnS QD	2.715 ± 0.002	0.089 ± 0.016 0.058^a [11] 0.140^a [12]	15 ± 2 13 [11] 23 [12]	5.13 3.83^a [11] 5.20^a [12]	0.39 ± 0.01 0.41^a [1], 0.32^a [2], 0.37^a [3,11], 0.57^a [8]
InP nanowires	1.50 [20]	0.090^a [20]	20.5 [20]	3.78^a [20]	0.006^a , at 30 K [20]
Bulk InP	1.42 [15,25]	0.049^a [25]	13.8^a [25]	3.06^a [25]	0.008^a , at 6 K [25] 0.002 , at 5 K [26] 0.012 , at 300 K [26]

^a our estimate using data from the cited work

The temperature influence on optical absorption spectra of crystalline media is also exhibited as the change of a characteristic band FWHM. Figure 2(b) involves the normalized OA spectra of the InP/ZnS QDs at various temperatures, as well as their photoluminescence spectrum at 296 K. An important point that needs to be made here is that the low-energy edge of the exciton absorption peak shifts towards higher energies as T drops with its slope remaining unchanged. The fact described is explained by the constancy of the band shape with temperature, as clearly illustrated in the insert of Fig. 2(b), where the maxima of the normalized exciton bands are combined into a single point E_m . On the other hand, authors of [11, 12] observed an increase in the width of the PL bands for the InP/ZnS QDs with increasing temperature. In particular, for the sample having the commensurable value of luminescence FWHM ≈ 0.24 eV at 300 K, the homogeneous broadening amounts to $\Delta\text{FWHM}(T) \approx 0.08$ eV in the temperature range of 2 – 300 K. It should be noted that we are not aware of works concerned with temperature behavior of the first exciton absorption peak

in InP/ZnS quantum dots. For bulk InP single crystal the discussed shift amounts to $\Delta E_1(T) = 0.08$ eV in the 5 – 300 K range and FWHM is changed in the 0.002 – 0.012 eV diapason [26]. Such behavior – $\Delta E_1(T) \gg \Delta \text{FWHM}(T)$ – accords pretty well with the results of our work. In this regard, we consider the observed temperature shift of 0.11 eV for the exciton absorption peak on the background of a temperature-independent FWHM as an important experimental result requiring further investigation.

The paper estimates the FWHM in two ways. The first approach calculates the half width at half maximum (HWHM) value in a direct manner, graphically, through the visible low-energy wing of the experimental absorption band, see Fig. 2(b) (insert). The FWHM is calculated as twice the HWHM then. Moreover, we used it to analyze independent data by other researchers, see Table 1. The FWHM value derived is typical of the InP/ZnS QDs with $E_1 = 2.49 - 2.68$ eV and dramatically exceeds the value for the InP bulk samples (see Table 1). The second technique is to approximate the low-energy side of the peak using the Gauss function under assumption of a negligible contribution of the various processes mentioned previously (see a red dashed line in Fig. 2(b)). Centers of the Gaussians are fixed at the E_1 values calculated by second derivative processing of the corresponding OA spectrum. The FWHM obtained this way equals to 0.29 ± 0.01 eV.

The lack of temperature-dependent broadening of the exciton absorption peak highlights its inhomogeneous character. The authors of the paper [9] point out the dominant contribution of the inhomogeneous broadening to the total width of the band for the InP/ZnS QD. They conclude it by analyzing the stationary absorption and luminescence spectra in terms of the Kennard–Stepanov relation. The composition and thickness of the layers in the multiple quantum wells are also known to influence inhomogeneous width of the exciton absorption peak [27]. Noteworthy that temperature independent behavior under discussion is observed not only in low-dimensional systems and is typical for statically disordered solids [28, 29]. Properties of the optically active point defects in amorphous and glassy structures are significantly affected by inhomogeneous broadening resulting from the site-to-site non-equivalence of the local center environment [30]. By analogy with the above mentioned, non-equivalence of excitons generated by photon absorption can be considered for the case of studied QD. It is associated with the distribution in size, shape, imperfections, etc., revealing itself in strong differences of lattice potentials of each individual nanocrystal in the ensemble. These variations lead to the inhomogeneous broadening of the exciton absorption band.

Thus, using the second-order derivative spectrophotometric method, we performed estimates of the optical transition energies ($E_1 = 2.60 \pm 0.02$ eV, $E_2 = 4.70 \pm 0.02$ eV) for InP/ZnS colloidal quantum dots at room temperature. It is shown that the values obtained are independent on the QD solution concentration ranged from 40 to 0.04 g/l. The value of E_1 corresponds to a first exciton absorption peak of the InP core, and E_2 can be attributed to transitions in the ZnS shell. The temperature dependence of E_1 within $T = 6.5 - 296$ K range was investigated for the first time. Also, we analyzed the experimental results in frame of a linear model and using Fan's expression. The temperature coefficient $\beta = 4.76 \cdot 10^{-4}$ eV/K in the range of $T = 90 - 296$ K corresponds to the value of a similar parameter for the InP bulk crystals. It is found that the change of the E_1 energy with temperature is mainly due to the interaction between excitons and longitudinal acoustic phonons ($\hbar\omega = 15$ meV). In addition, we established that the peak's FWHM equals to 0.39 eV remains unchanged within the specified temperature range, which highlights the inhomogeneous origin of broadening and a high degree of static disorder in the ensemble of the QDs studied.

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